

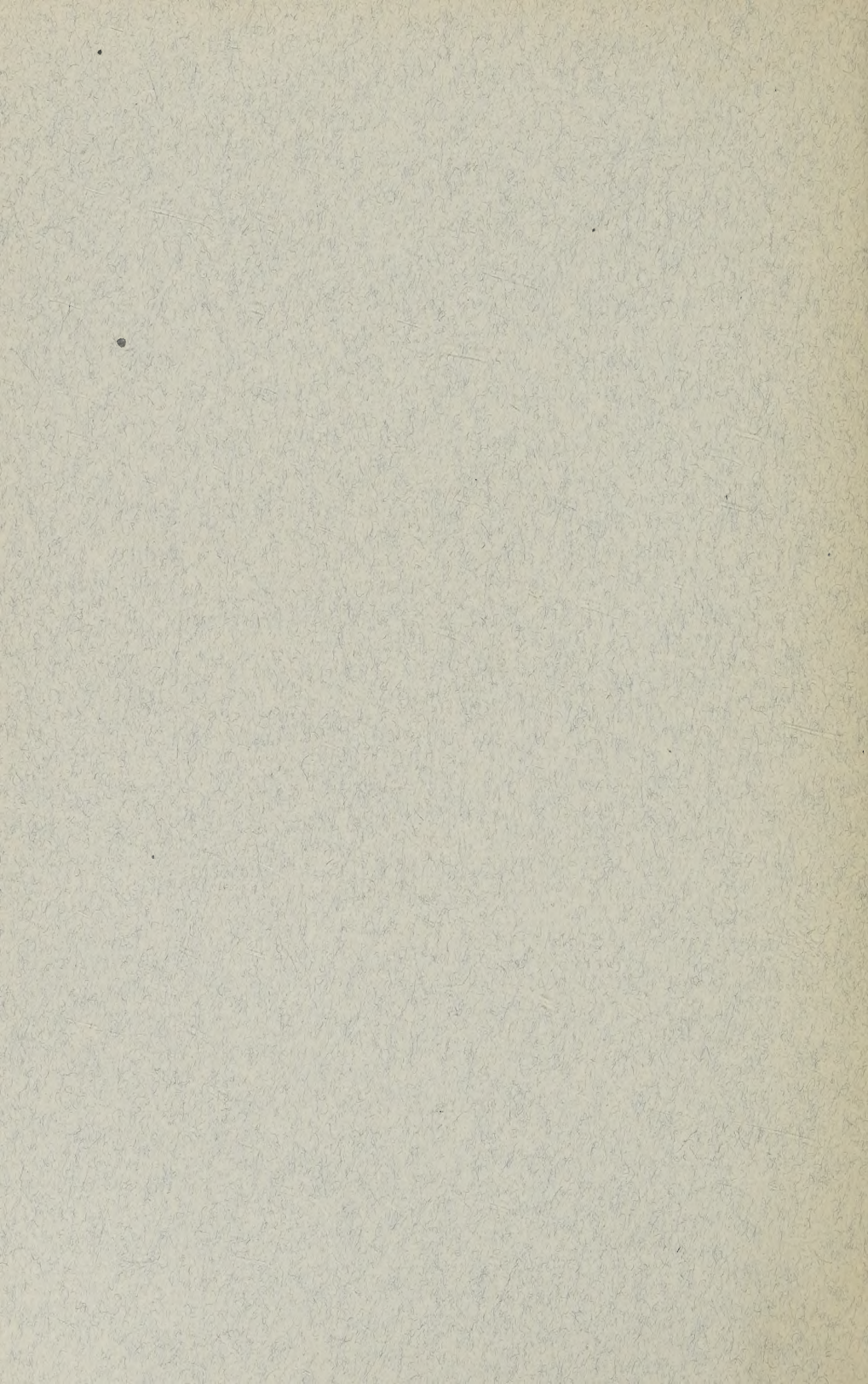
A Study of the Catalytic Conversion of Blue Water Gas to a Gas of High Methane Content

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

By
Frank Weldon Hightower
Ann Arbor
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Synthesis of Methane from Water Gas^{1,2}

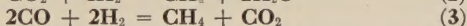
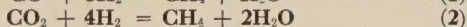
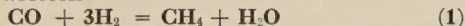
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ANN ARBOR, MICH.

This paper presents the results of a study of the conversion of mixtures of CO_2 , CO , and H_2 to CH_4 and other products at temperatures of $280\text{--}370^\circ\text{C}$. while at atmospheric pressure and in presence of a nickel catalyst. The results are in general agreement with other investigators in showing the formation of large proportions of methane from gases containing CO , H_2 , CO_2 , and H_2O within fairly wide limits of composition.

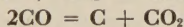
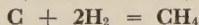
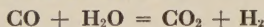
The decomposition of CO according to the equation
$$2\text{CO} = \text{C} + \text{CO}_2$$
appeared to a small degree at $300\text{--}370^\circ\text{C}$., but was somewhat erratic in quantity. It is suggested that the decomposition may be autocatalytic since the decomposition appeared to be less with new catalysts.

The path of the reaction as between the three equations usually written



depends upon a number of conditions. Reaction (2) appears to be uncomplicated. The question as to whether (1) or (3) dominates is largely a function of the water vapor present. Water vapor represses (1) to a marked extent. If conditions are arranged so that the water vapor is removed at intervals during the conversion, reaction (1) predominates.

The equilibrium constants obtained from this experimental work are compared with those calculated from published data on the reactions.



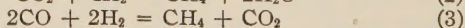
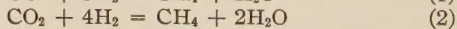
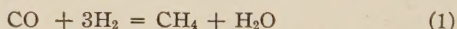
The most probable values calculated in this way for $\log K$ of the combined reactions vary from 19.4 to 22.24 at 350°C . The highest value we have obtained experimentally is 19.6 and the experimental results are in general below the theoretical.

¹ Presented before the Division of Gas and Fuel Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

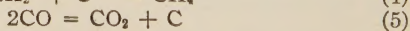
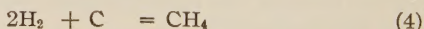
² This paper forms a part of the dissertation submitted by Mr. Hightower in partial fulfilment of the requirements for the Ph.D. degree at the University of Michigan.

ALL efforts to synthesize methane from carbon monoxide or carbon dioxide and hydrogen reacting in the gas phase failed until Sabatier and Senderens^{1,*} took up this problem in 1896 in the course of studies of the catalytic effects of finely divided metals on gas reactions. They soon determined that, the conditions of preparation being equal, catalysts of nickel had a more pronounced effect than catalysts of other metals. The possibilities of industrial utilization of such hydrocarbon syntheses were recognized and numerous records in the patent literature attest to attempts to carry out the synthesis of methane on an industrial scale. As this provides a method of converting a non-combustible gas (CO₂), as well as a gas of low-heating value (CO), into a hydrocarbon gas of high-heating value, the processes were naturally first applied to the various forms of artificial consumers' gas, such as illuminating gas and water gas.

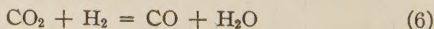
Within a few years of the publication of Sabatier and Senderens' first work¹ other investigators had turned from the commercial applications of the synthesis to the chemical principles underlying the reactions. Attempts were made to follow the course of the reactions, determine the conditions for optimum production of methane, and formulate the energy relationships involved. At intervals since about 1910 further work along these lines has been reported. The investigations of Sabatier and Senderens;¹⁻⁴ of Mayer with Altmayer,^{5,7,10} with Henseling⁶ and with Jacoby;^{8,9} of Jochum;¹¹ of Armstrong and Hilditch;^{12,13} of Haslam and Forrest;¹⁴ and of Neumann and Jacob¹⁶ may be cited as of particular interest. The equations usually written for the synthesis of methane are as follows:



Some of these investigations are of interest mainly from the industrial application; a second class includes direct measurements of equilibrium at a definite temperature in one of the reactions noted above; and a third group contains studies of equilibria in reactions other than those cited above, but furnishing data which permit the calculation of equilibrium constants for one or more of these reactions. Investigations of the second and third groups should provide valuable checks upon the trustworthiness of the experimental data secured. Mayer, with Altmayer and Jacoby,^{5,7-9} published a series of researches upon the equilibria in the reactions



Cantelo¹⁷ also has recently published data on the equilibrium of (4). Equilibrium data for the water-gas reaction



* Numbers in text refer to bibliography at end of article.

is also available. From these equilibria the equilibrium for the three methane-synthesis reactions may be calculated. Direct measurements of the equilibrium constants for reactions (1) and (2) have been published only by Neumann and Jacob.¹⁶ Other published measurements of equilibrium constants and studies of catalytic synthesis of methane will be mentioned in the sections to follow.

Apparatus

The apparatus for the experimental work consisted of a Pyrex glass tube containing the catalyst supported in an electric furnace. The temperature of the catalyst was obtained by thermocouples inserted in the tube and the temperature of the furnace was controlled by an electrical controller. The apparatus for circulating the gas has been described in a previous paper.[†]

In the first apparatus the tube was vertical and the gas passed upward through a layer of broken porous porcelain 4 inches (10 cm.) long placed within the heated furnace. In the second apparatus the tube was horizontal and the gas on entering passed through a 17-inch (43-cm.) length of packed tube, 12 inches (30 cm.) of this being inside the furnace. A perforated porcelain plate separated the catalyst from the gas entrance section of the tube. The catalyst section was 6 inches (15 cm.) long, with a volume of 75 cc. The hot junctions of the thermocouples were situated on the axis of the tube in the middle of the catalyst section. The exit section was packed with broken unglazed porcelain. The three thermocouples, insulated with Usalite sheathing, were led out the exit tube. The thermocouple wires were separately threaded through a rubber stopper fitted to the opening of this tube and the glass-to-rubber joint was covered with a viscous glue-wax coating as described below. The resulting seal gave no evidence of leakage at any time. The gas exit was connected to the water-collection bulb and lines leading to the circulation pump.

Catalysts

All catalysts used in this work consisted of nickel supported on unglazed porcelain. Pieces of unglazed porous plate screened between 10 and 14 mesh were soaked in a concentrated water solution of high-grade nickel nitrate. The percentage of metallic nickel in the finished catalyst varied between 1.3 and 4.9 per cent. The water was driven off from the catalyst by heating at 95–100° C. and the nitrate was decomposed according to one of the following methods:

(A) The porcelain-nickel nitrate product was decomposed by heating in a current of hydrogen, the temperature being maintained at about 200° C. for 2 hours, then raised gradually to 350° C., and finally held at 400–410° C. for 5 hours. At the end of this period the catalyst was allowed to cool in a current of hydrogen. The catalyst was found to be active, and no further reduction of the nickel was sought.

[†] *Ind. Eng. Chem.*, **20**, 99 (1928).

(B) The nickel nitrate-porcelain material was heated in a current of air for 6 hours, the temperature being raised gradually to 460° C., then allowed to cool in air. When at room temperature the air was swept out by hydrogen and the nickel oxide-porcelain material was heated in a current of hydrogen. A temperature of 200–250° C. was maintained for 4 hours. The reduced catalyst was allowed to cool in hydrogen.

The catalysts prepared by both these methods were active and no definite distinction can be made between them.

Preparation of Gases

The carbon dioxide and hydrogen were taken from commercial cylinders without purification. Carbon monoxide was prepared by dropping formic acid (85 per cent solution) into concentrated sulfuric acid heated to between 95° and 120° C. according to the method of Rupp.¹⁹ The gas was passed through a short scrubbing tube containing 20 per cent sodium hydroxide solution to remove acid spray. No attempt was made to remove completely the small amount of carbon dioxide in the gas. The gases were in all cases thoroughly mixed and the samples for analysis were taken immediately before the commencement of the test.

Gas Analysis

The gases were analyzed by ordinary absorption methods for carbon dioxide, unsaturated hydrocarbons, oxygen, and carbon monoxide; and hydrogen and methane were determined by explosion, and nitrogen was estimated by difference. In some cases the copper combustion method was used for determination of hydrogen and methane, but the values were all checked against determinations by the explosion method. The copper oxide-combustion method was found to give reliable values for methane only when the gas analyzed contained less than about 5 per cent CH_4 . The gas burets were filled with mercury. Analyses by the absorption method are accurate to within about 0.2 per cent. The compositions of methane, hydrogen, and nitrogen may be about 2 per cent in error.

The quantity of water vapor in the initial gases was calculated from the temperature of the water saturator and that in the product gases was calculated from the differences in weight of the calcium chloride tubes.

Experimental Procedure

The experiments were carried out in two distinct groups, those with the single pass and those with multi-passes. All of them were carried out at substantially atmospheric pressure. A pressure of 5 to 20 mm. above atmospheric was maintained throughout the system in all runs, to avoid the possibility of drawing air into the system. The effect of such a pressure increase, less than 0.03 atmosphere, upon the course of the reactions would be too slight to be noted. All reported gas volumes are computed from the observed data to a pres-

sure of 760 mm. and a temperature of 0° C. Water is calculated as vapor under these conditions. In the single-pass tests several liters of the gases were passed through the system, the initial and final water content and the initial and final gas compositions being determined. In the multi-pass series several liters of gas were also used and the temperature of the furnace was held constant throughout all the passes, as was also the temperature of the water saturator at the inlet. The gases cooled to atmospheric temperature between each pass and therefore the water vapor formed in each pass was removed. The effect of this difference in procedure will be discussed later.

Certain expressions employed in reporting the results of the experiments should be defined. The "H₂:CO ratio" refers to the relative volume proportions of hydrogen and carbon monoxide in the synthetic blue water gas used, the "initial" gas. The term "conversion ratio" is used to indicate the extent to which carbon monoxide and carbon dioxide of the initial gas were reduced to methane. The value of the conversion ratio for each test was set equal to the fraction

$$\frac{\text{Volume of CH}_4 \text{ in product} - \text{volume of initial CH}_4}{\text{Sum of volumes of initial CO and CO}_2}$$

The rate of flow of a gas through a catalyst is expressed in terms of "space velocity." This commonly adopted unit may be defined as: unit volume of gas, measured at the catalyst exit, passing through unit apparent volume of catalyst in one hour.

Conversion as a Function of Temperature

The study of the effect of temperature upon conversion of blue water gas components to methane was restricted to the range 280° to 377° C. Methane is formed from carbon monoxide and hydrogen at temperatures above and below this range, but the higher yields are obtained from catalytic reduction within the specified limits.

Table I—Effect of Temperature on Conversion of Hydrogen and Carbon Monoxide to Methane

RUN	TEMPERATURE ° C.	SPACE VELOCITY	INITIAL H ₂ :CO RATIO	LOSS IN GASEOUS CARBON Per cent	CON- VERSION RATIO	CH ₄ IN PRODUCT Per cent
70-A	285	24.0	1.35	0	0.12	6.1
69-B	293	25.7	1.63	0	0.37	22.3
71-A	300	24.9	1.35	8.9	0.55	55.0
68-A	342	30.0	1.33	19.0	0.60	63.1
67-A	350	30.0	1.33	3.0	0.73	72.1
76-C	352	12.4	1.26	14.3	0.62	65.6
56-B	355	14.4	1.34	9.5	0.65	57.5
56-D	365	15.9	1.34	12.9	0.62	56.3
75-A	377	19.3	1.53	1.1	0.49	52.8

The effect of increasing temperature is shown in Table I. The gas used was synthetic blue water gas prepared in the laboratory as already described, with a ratio of H₂ to CO varying from 1.26 to 1.63. The space velocity varied from

12.4 to 30.0, giving a time of contact of from 2 to 5 minutes. There is no deposition of carbon below 300° C. and above that temperature variable amounts are formed. It will be noted in Table I that minimum amounts of free carbon are formed in tests 67-A and 75-A. The catalyst in 67-A had been used previously but had been given a new reduction in hydrogen just before this test. The catalyst of 75-A was used for the first time. This smaller amount of carbon deposited when a fresh catalyst was used makes it probable that the deposition of carbon is autocatalytic. The results are plotted graphically in Figure 1, on which all the conversion values of Table I are represented. The points which are distinctly below the curve, 68-A and 76-C, are those which show large deposition of carbon, 19.0 and 14.3 per cent, respectively.

The ratio of CH_4 formed to initial CO_2 and CO , as given in Table I, shows a maximum conversion ratio of 0.73 in test 67-A at 350° C. In this test the volume of the initial

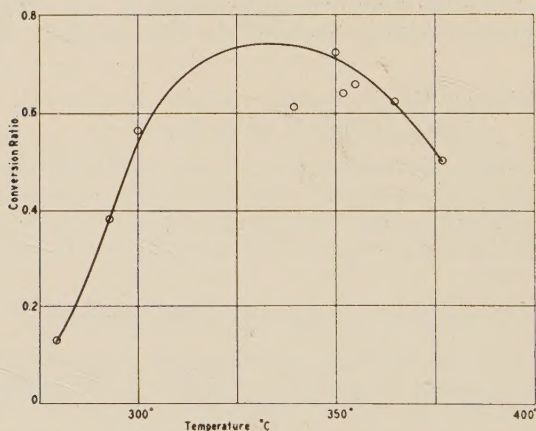


Figure 1—Conversion to Methane as a Function of Temperature

gas was 750 cc. with 0.5 per cent CO_2 and 39.3 per cent CO , giving a total volume of CO_2 and CO of 299 cc. It contained no CH_4 . The product gas measured 306 cc. and contained 72.1 per cent of CH_4 , giving a volume of 220 cc. The conversion ratio was therefore 0.73. It has been noted that the catalyst was freshly reduced before this test and that this may account for the small amount of free carbon formed and the higher conversion to CH_4 . These results do not necessarily show equilibrium conditions, although the time of contact is relatively long. They are merely the results obtained under the conditions of our tests. They confirm in general the work of Neumann and Jacob, who state that there is no carbon deposition below 303° C. but that carbon deposition takes place in increasing amounts at higher temperatures; but the fact that in test 75-A only 1.1 per cent of the car-

bon gas was decomposed to form carbon when using a fresh catalyst at 375° C. indicates that caution should be used in generalizing.

Recirculation Tests

The question as to which of the two reactions, (1) and (3), was the primary one under the conditions studied could be answered, in part at least, by a technic which removed the water from the reaction. It was not possible to do this completely, but an apparatus was arranged which attained this end in considerable measure.

The initial gas was recirculated rather rapidly through the catalyst tube and allowed to cool to room temperature after each pass through the catalyst. Thus it entered the catalyst each time saturated with water at room temperature. The change in volume was measured and samples were withdrawn for analysis at intervals during the recirculation process. Two series of runs of this sort were made, No. 87 at 302° C. with 30 passes and No. 88 at 350° C. with 110 passes. The catalyst was not disturbed during these two series. Since the reaction took place in a glass tube, it was possible to make a visual examination of the catalyst after each series. At the end of series 87 there was a brown discoloration at the exit of the catalyst tube and a mirror-like deposit on the glass at the beginning of the heated section of the inlet end. The catalyst had changed in color at the inlet end from its normal gray to the white of the porcelain support. At the end of test 88 these phenomena were more noticeable. When the catalyst was removed, the deposition of carbon was evident and it was shown that the mirror consisted of nickel.

Table II—Effect of Recirculation of Gas over Catalyst:
Series 87 at 302° C.

GAS COMPONENT	NUMBER OF PASSES OVER CATALYST WHEN SAMPLED				
	0	3	15	20	30
	%	%	%	%	%
CO ₂	0.9	1.5	3.3	5.7	4.3
CO	43.2	44.0	45.3	46.1	47.0
CH ₄	0.0	3.6	12.3	17.2	24.5
H ₂	53.3	47.8	36.2	29.2	21.1
N ₂	2.6	2.7	2.5	1.8	2.0
Ratio H ₂ :CO	1.23	1.11	0.89	0.56	0.45
Conversion ratio		0.07	0.20	0.24	0.30
Volume, cc.	5560	5075	4050	3476	3014

Test 87 was made with a synthetic water gas with 53.3 per cent H₂ and 43.2 per cent CO at a temperature of 302° C. The gas was circulated 30 times over the catalyst with a space velocity of about 400 at each pass. Volumes were measured and analyses made at five different periods. The data are presented in Table II. The striking thing about the gas composition at the various stages is that CO₂ remains small and the CO, which starts at 43.2 per cent, increases to even higher percentages, while the CH₄ rises from 0 to 24.5 per cent. The carbon balance shows a formation of free carbon amounting at the end of the 30 passes to 6.9 per cent

of the initial gaseous carbon present, which is equivalent to 0.23 per cent per pass. The apparent path of the carbon which has changed its form may be calculated as follows:

		INITIAL CO ₂ + CO Per cent
2CO = C + CO ₂	(5)	13.8
CO + 3H ₂ = CH ₄ + H ₂ O	(1)	26.1
CO ₂ + 4H ₂ = CH ₄ + 2 H ₂ O	(2)	3.6
		43.5

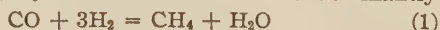
Test 88 was made in a way similar to 87 at a higher temperature, 350° C., and with a total of 110 passes. The data are presented in Table III. As in test 87, the percentage of CO₂ remains low and the CO varies little from its initial value of 48.6. The apparent path of the reactions may be calculated as follows:

EQUATION	INITIAL CO ₂ + CO Per cent
(5)	28.0
(1)	16.3
(2)	8.0
	52.3

Table III—Effect of Recirculation of Gas over Catalyst:
Series 88 at 350° C.

GAS COMPONENT	NUMBER OF PASSES OVER CATALYST WHEN SAMPLED						
	0	1	5	30	50	78	110
	%	%	%	%	%	%	%
CO ₂	1.3	2.0	3.1	5.7	7.7	7.8	8.9
CO	48.6	49.3	47.0	49.3	48.3	47.9	45.8
CH ₄	0.0	3.5	8.1	19.1	22.0	28.9	30.8
H ₂	46.5	42.5	34.8	22.1	16.2	9.3	7.2
N ₂	3.6	2.7	6.5	3.7	5.7	5.9	6.5
Ratio H ₂ :CO	0.96	0.86	0.74	0.47	0.34	0.19	0.16
Conversion ratio		0.03	0.14	0.24	0.25	0.30	0.29
Volume, cc.	5740	5496	4850	3610	3270	2980	2785

The errors in gas analysis are too great to follow the reactions quantitatively from one pass to another, but calculations show that the path of the reactions stays fairly constant through the series and is unaffected by the changing ratio of H₂ to CO. The dominant reaction is (1), with (5) furnishing the CO₂ for (2). The dissociation of CO is apparently uninfluenced by the relative proportions of H₂ to CO. The percentage of CH₄ does not rise above 31 per cent and at the end of the run in Table III is changing very slowly and apparently reaching a steady state. The composition of the initial gas was manifestly incorrect to obtain high values of CH₄. Since the reaction is dominantly

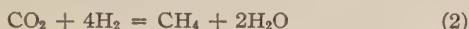


it is evident that the initial gas should have had three molecules of H₂ to one of CO instead of having approximately one molecule of each, if the maximum conversion was to be obtained.

Influence of Water Vapor

The results of the tests where the water vapor was removed at the end of each short contact have been discussed under the head of Recirculation Tests. The following discussion,

deals with tests in which the gas stayed in contact with the catalyst for a longer time and the water vapor formed in the reaction remained throughout the single slow pass. Tests 101, 102, and 103-A were all made from synthetic blue water gas at 350° C. and at space velocities of about 16. Comparison of the initial and final gas compositions is given in Table IV. The outstanding difference between these figures and those of Tables II and III is in the percentage of CO. Whereas in Tables II and III this was almost the same in the initial gas as in the final gas, the percentage of CO in the gases of Table IV drops to less than 3 per cent in every case. The CO₂ in Tables II and III does not increase above 7 per cent in the final gases, but in Table IV it rises to high figures. The presence of so much water vapor, as might have been expected, has inhibited the reaction



so that the dominant reaction becomes



Neumann and Jacob found very small amounts of CO₂ formed even at 450° C. while Haslam and Forrest found large amounts of CO₂ at temperatures even below 300° C. This difference is due partly to the fact that Neumann and Jacob always had more than 3 molecules of hydrogen for each molecule of carbon monoxide in their gas, while Haslam and Forrest worked with a gas containing only 1.5 molecules of H₂ for each molecule of CO. Our results confirm those of Haslam and Forrest when working under their conditions.

Table IV—Changes in Composition of Gases on Single Slow Pass
(Temperature, 350° C.)

GAS COMPONENT	TEST 101		TEST 102		TEST 103-A	
	Initial	Final	Initial	Final	Initial	Final
	%	%	%	%	%	%
H ₂ O ^a	2.7	32.8	7.5	28.2	2.8	9.5
CO ₂	1.9	17.3	2.1	20.2	0.4	39.4
CO	32.3	2.7	33.2	2.1	48.4	2.6
CH ₄	0	33.2	0	28.9	0	39.7
H ₂	56.6	7.6	50.1	11.7	45.6	4.5
N ₂	6.5	5.6	7.0	8.9	2.6	3.7
Total volume, cc.	1945	1236	2264	1422	3140	1709
Space velocity	16.8		14.8		16.1	

^a Calculated as vapor at atmospheric temperature.

Reaction between Carbon Dioxide and Hydrogen

The behavior of a mixture of CO₂ and H₂ was tested in two runs—104 and 105—at 350° C. The gas compositions are given in Table V. Carbon monoxide was absent from the initial gas and is reported in such small amount in the final gas that it may be an error of analysis. The reaction proceeds without complication according to reaction (2). This confirms the work of Sabatier, Mayer and Henseling, and Neumann and Jacob.

Table V—Changes in Composition of Gases Consisting Mainly of CO₂ and H₂ on Single Slow Pass over Nickel Catalyst at 350° C.

GAS COMPONENT	TEST 104		TEST 105	
	Initial	Final	Initial	Final
	%	%	%	%
H ₂ O	3.0	47.5	8.4	44.3
CO ₂	18.8	4.4	21.5	11.1
CO	0	0.1	0	0.2
CH ₄	0	25.9	0	20.3
H ₂	76.4	19.7	68.7	22.1
N ₂	1.4	2.1	1.6	1.8
Volume, cc.	3100	1941		

Path of the Reactions

It has been stated that the path of reaction (2) seems attended with no side reaction. It is otherwise, however, with the reactions which cause the formation of CH₄ from CO. The reaction (3) may be derived by addition of equations (6) and (1). So also an equation can be written involving the formation of CH₄ from CO and H₂O



This in turn may be built up from (3) and (6).

The heats of reactions and the free energies at 20° C. indicate the strong tendency of all these reactions to go to the right. It is thus impossible to calculate the exact path of the reaction, and in the discussions here the equations (1), (2), and (3) have been used because they have been generally accepted in the literature.

Calculation of Data on Equilibria

For those runs in which determinations of the CH₄, CO₂, CO, H₂, and H₂O in the product gases were obtained, the partial pressures of these components could be calculated and used in computing the value of equilibrium constants for the reactions involved in methane formation. Without attempting to differentiate between the three equations (1), (2), and (3), or to specify the part each played in reaching the final equilibrium, an equation containing all five of the reactants may be used. The sum of equations (1) and (2) gives such a relationship



The equilibrium constant for equation (7), stated in terms of the partial pressures of the components, is

$$K_7 = \frac{(\rho\text{CH}_4)^2 (\rho\text{H}_2\text{O})^3}{(\rho\text{CO})(\rho\text{CO}_2)(\rho\text{H}_2)^7} = K_1 \times K_2$$

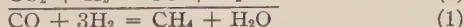
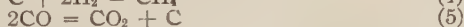
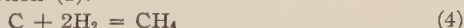
Table VI gives values of log₁₀ K_p calculated from the data of a number of runs, according to equation (7). It may be assumed that the highest values of K_p, or its function log₁₀ K_p, represent the nearest approach to equilibrium conditions in the experiments; that is, reaction will not go beyond equilibrium.

Table VI—Experimental Determination of Equilibrium Constant for Reaction (7)

(Temperature, 350° C.)		
RUN	SPACE VELOCITY	$\log_e K_p$
101	16.8	17.9
102	14.8	14.2
103-A	16.1	19.6
103-B	21.0	17.9
104	17.5	16.4

The only published experimental data on K_p for reactions (1) to (3) at lower temperatures is contained in the work of Neumann and Jacob.¹⁶ Their research presented data on equations (1) and (2) over a temperature range of about 800 degrees, from 300° to 1050° C. Their experimentally determined values for the equilibrium constant of reaction (1) were in agreement with the calculated values in the range 860° to 1050° C.; for lower temperatures no values of K_p were published and a recalculation of their results indicates that they did not reach equilibrium at the lower temperatures. Neumann and Jacob appear to have assumed that H_2O was produced from CO and H_2 under their conditions of experiment in amount equal to the CH_4 produced. This assumption was necessary in deriving the partial pressures for K_1 from their data, but it is certainly not warranted in a study of methane formation from blue water gas.

Various combinations of equations (4), (5), and (6) may be added or subtracted to give the equations for the methane-forming reactions (1), (2), and (3). Their equilibrium constants (K_p) may be similarly combined and from such calculations the values of K_p for (1), (2), and (3) may be obtained. For instance, addition of reactions (4), (5), and (6) yields reaction (1).



Therefore the product of K_4 , K_5 , and K_6 is equal to K_1 . Similarly, reaction (2) is equal to the sum of reactions (1) and (6) and the product of K_1 and K_6 is equal to K_2 . K_7 can then be expressed in terms of K_4 , K_5 , and K_6 instead of K_1 and K_2 .

$$K_7 = K_1 \times K_2 = K_4 \cdot K_5 \cdot K_6 \times K_4 \cdot K_5 \cdot K_6^2 \\ = K_4^2 \cdot K_5^2 \cdot K_6^3$$

The published experimental data on the equilibrium constants for equations (4), (5), and (6) have been used to compute the theoretical values of the equilibrium constant for equation (7) at the temperatures of the experiments reported here. Table VII presents this material. The references cited in this table contain equations suggested by the different workers to represent their data; these equations were used in computing the values of $\log_e K$ at the temperatures indicated for the reactions.

The values of $\log_e K_4$, $\log_e K_5$, and $\log_e K_6$ for the desired temperature are used in the expression

$$2 \log_e K_4 + 2 \log_e K_5 + 3 \log_e K_6 = \log_e K_7$$

Equilibrium constants so computed, for temperatures of 302° and 350° C., are listed in Table VIII. It will be seen that the value of $\log_e K_7$ obtained by use of Mayer and Jacoby's⁹ data on reaction (5), Cantelo's¹⁷ on reaction (4), and Haber's³⁰ on reaction (6) yields the value of 19.37 for $\log_e K_7$ at 350° C. Use of the values determined indirectly by Eastman and Evans²⁹ in place of Haber's data gives $\log_e K_7$ at 350° C. = 22.24.

Table VII—Comparison of Equilibrium Constants $\log_e K_p$ for 623° K.

SOURCE OF DATA	REACTION (4)	REACTION (5)	REACTION (6)
	$K_p = \frac{(p\text{CH}_4)}{(p\text{H}_2)^2}$	$K_p = \frac{p\text{CO}_2}{(p\text{CO})^2}$	$K_p = \frac{(p\text{CO})(p\text{H}_2\text{O})}{(p\text{CO}_2)(p\text{H}_2)}$
Lewis and Randall ²⁶ equation	+4.64	+12.18	-3.27
Saunders ²⁷ equation	+4.97	+12.30	
Mayer and Altmayer ^{6,7} equation	+5.20		
Mayer and Altmayer ⁷ data	+5.23 ^a		
Cantelo ¹⁷ equation	+2.50		
Mayer and Jacoby ⁹ equation		+12.11 ^b	
Mayer and Jacoby ⁹ data		+12.15 ^c	
Neumann and Jacob ¹⁸ equation		+5.64 ^d	-2.81 ^e
Mayer and Altmayer ¹⁰ equation			-3.40
Eastman and Evans ²⁹ data			-2.45 ^f
Haber and Richardt ³¹ equation			-3.40
Engels ³² equation			-3.12
Hahn ³³ equation			-3.33

^a Determined graphically from Mayer and Altmayer's tabulation of partial pressures.

^b Using 7.92 for "I" in equation $(\text{C}/2 + \text{CO}_2/2 = \text{CO})$ and multiplying entire $\log_e$ equation by 2.

^c Estimated graphically from plot of Mayer and Jacoby's data, tabulated by them to 500° C.

^d Using 8.75 for "I" in equation $(\text{C} + \text{CO}_2 = 2\text{CO})$.

^e Values given for K at 786–1086° K. plotted and curve extrapolated to 575° K.

^f Values of K plotted from data given and curve extrapolated to 575° K.

Table VIII—Comparison of Values of Equilibrium Constant for $\log_e K_p$ for Reaction (7)
(Temperature, 623° K.)

RUN	$\log_e K_p$		INVESTIGATOR		
	Exptl.	Calcd.	Reaction (4)	Reaction (5)	Reaction (6)
101	17.97	19.02	Cantelo	Mayer	Eastman
103-A	19.6	19.37	Cantelo	Average ^b	Haber
103-B	17.9	22.24 ^a	Cantelo	Average ^b	Eastman
104	16.4	23.43	Lewis	Lewis	Lewis
		27.72	Mayer	Saunders	Eastman

^a Most recent data.

^b Average of values from Saunders, Lewis, and Randall, and Mayer and Jacoby.

The minimum amount of hydrogen to react stoichiometrically is a volume equal to the carbon monoxide and four times as great as the carbon dioxide. Any larger proportion of hydrogen up to three times the volume of the carbon monoxide and four times the hydrogen should be taken care of by equation (7).

The highest value for the equilibrium constant obtained in our work was 19.6 in run 103-A, obtained with a new catalyst at a space velocity of 16 and with a gas composed of almost equal volumes of CO and H₂. In this test there was a decomposition of CO to form CO₂ and C, which amounted to 8.6 per cent of the total carbon present. If this decomposition took place before the gas traversed the catalyst, it would have no influence on the value of the equilibrium con-

stant. However, it is probable that this thermal decomposition of CO took place while the gas was traversing the catalyst and therefore some of the CO₂ formed did not have time to react with the H₂ before leaving the catalyst. This would cause the equilibrium constant as determined experimentally to be lower than the theoretical.

Working with an entirely different initial gas, CO₂ and H₂, the equilibrium constant calculated in the same manner from the data of test 104 gives a value for the constant of 16.4. It is therefore believed that our results fall somewhat short of the calculated equilibrium conditions. However, in view of the varied possibilities of the reactions, it will be very difficult consistently to reach a result which may be definitely stated to represent equilibrium conditions.

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Apparatus for Storing and Circulating Gases^{1,2}

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THE study of gas reactions often requires equipment for circulating and storing gases. The weight and expense of mercury makes this liquid objectionable as a containing liquid when volumes of more than a few hundred cubic centimeters are to be used. The apparatus described herein, which uses only small volumes of mercury, has proved itself useful where contact with rubber is permissible and the contact does not have to be prolonged more than a few hours.

The gas-storage system consists of two rubber basketball balloons, each surrounded by water and contained in a large inverted bottle. The gas balloons are connected with each other through the pump and gas-circulating system, and the water bottles are connected with each other and with a reservoir of water carried on a small platform scale. The arrangement is shown in Figure 1. When this apparatus is used, gas is transferred from one balloon through the circulating apparatus and pump to the other balloon, while water flows directly from the bottle containing the second balloon to the bottle of the balloon being emptied. If there is no change in gas volume during this process, water merely flows from one balloon to the other and the weight of the reservoir of water on the scales does not change. On the other hand, any variation in gas volume will be detected at once without interrupting the flow of gas, through the change in weight of the water reservoir. The corrected volume of gas is computed from the weight of water and the temperature and barometric pressure. The error in reading a volume of 1 liter should not be over ± 0.3 per cent. The connections between the balloons and the pump are detailed in Figure 2. Gas from the circulating system enters through the three-way cock, *A*, and passes to either balloon 1 or 2. Gas from the other balloon passes to the inlet side of the pump through the three-way cock, *B*. A by-press, not shown in the drawing, permits the gas to be transferred from one balloon to another. Fused glass connections are not needed. If glass tubes are cut so that plane surfaces will be in close contact, a joint with good rub-

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² This paper forms part of the dissertation of Frank W. Hightower submitted in partial fulfilment of the requirements for the Ph.D. degree at the University of Michigan.

ber tubing may be made gas-tight by wiring the rubber tube and then smearing it with liquid glue, which is allowed to dry in the air until it loses its first stickiness and is then brushed with molten paraffin.

A general diagram of the whole equipment as applied to a study of the synthesis of methane from blue water

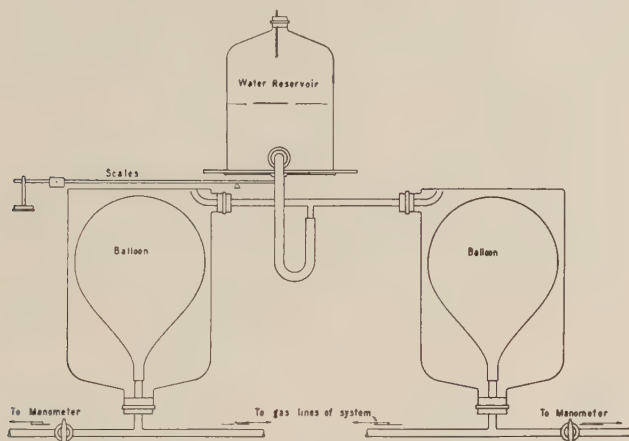


Figure 1—General Arrangement of Balloons and Scales

gas is given in Figure 3. When the first balloon was empty the gas flow was interrupted by stopping the pump; measurements of gas volume in the system were then taken and samples withdrawn for analysis. Where recirculation of the gases was desired, the positions of the two balloons in the order of flow could be exchanged in a few seconds by changing

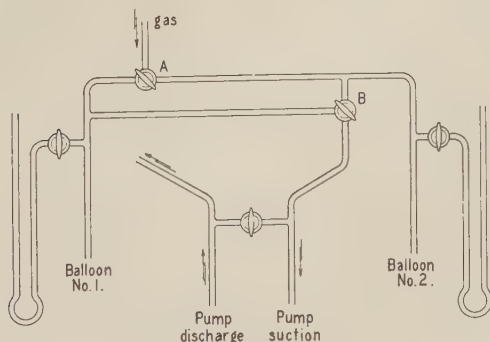


Figure 2—Detail of Connections in Gas-Circulation Apparatus

cocks and without interrupting the circulation of gas. The change was usually made at the instant the manometer of one balloon showed it to be empty.²

The gas-circulation pump is based upon the unit described by Chatterji and Finch,³ who used a mercury piston actuated

² *J. Chem. Soc. (London)*, **127**, 2464 (1925).

by a direct-driven plunger. The apparatus shown in Figure 4 utilized a standard bicycle pump to compress air whose pulsations actuated the mercury piston of the gas-circulation pump. The pump was connected by rubber tubing to the open side of the U-tube which contained the mercury piston. The plunger shaft was fitted with a piston head of two soft leather disks slightly larger than the inner cross section of the pump tube, and so placed as to act as a packing on both the suction and compression strokes. Positive seal at the piston head in the pump was insured by wetting the leather disks with a little olive oil at intervals of several weeks. One end of this rod was screwed into the end of the hollow shaft, forming a rigid extension of the shaft, the other end was fitted with a pin at right angles to its length. A reduction gear, driven by a motor and eccentrically connected, operated the piston. A series of holes at intervals along one radius of the reduction-gear wheel, into which the pin on the shaft fitted, allowed the stroke of the piston

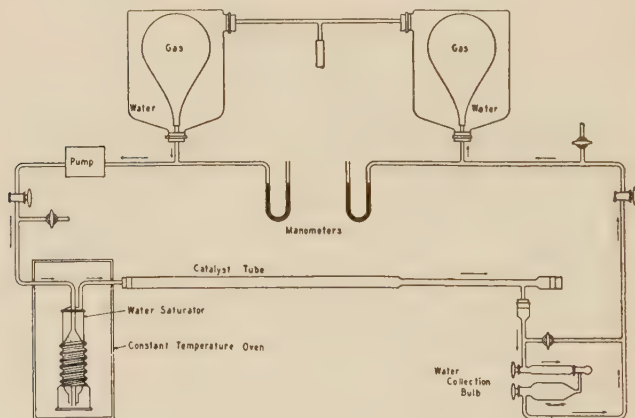


Figure 3—Apparatus as Used for Synthesis of Methane

to be varied from 1 inch to 7 inches (2.5 to 17.5 cm.). With the shortest stroke a volume of about 8 liters per hour was pumped. The maximum volume which could be pumped without throwing mercury out of the tube was about 60 liters per hour with this particular equipment, which had a mercury piston slightly less in diameter than the piston of the pump.

The pump may be mounted where convenient and connected by rubber tubing to the U-tube containing the mercury piston. On the compression stroke of the pump the mercury is depressed in the right-hand arm and raised in the left-hand arm of the U, compressing the gas above it. The compressed gas has two paths open to it, through the left-hand and right-hand traps. The outlet to the right-hand trap is, however, sealed by the mercury in the bottom, which is forced back into the capillary inlet tube. The gas therefore must bubble through the shallow mercury seal

of the left-hand trap. On the suction stroke it is the left-hand trap which is sealed while the gas flows with relatively little resistance into the pump chamber through the right-hand trap. The pump is effective for heads of less than 50 mm. of mercury and might readily be designed to work against higher pressures.

The only material error which may arise from the use of this equipment comes from solubility of the gases in the rubber balloons or from diffusion through the rubber. A

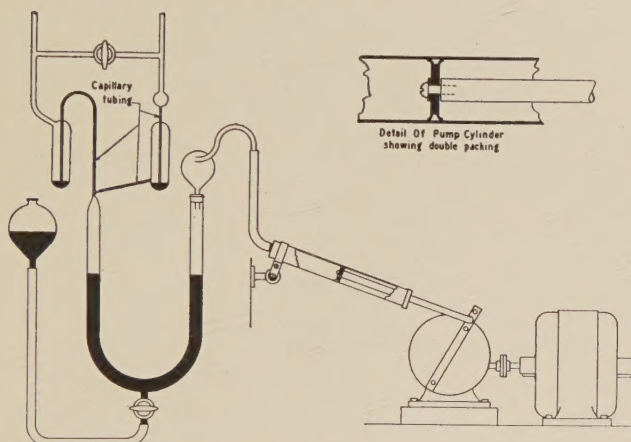


Figure 4—Details of Circulation Pump with Mercury Piston

gas mixture which initially contained 25.8 per cent carbon dioxide contained only 24.8 per cent after 12 hours and 23.7 per cent after 22 hours. After the water in the bottle surrounding the balloon had come into equilibrium with the gas content by standing 113 hours, further standing for 200 hours failed to show any measurable change in volume. Carbon dioxide diffused through rubber about eight times as fast as any of the other gases tested. Hydrogen, methane, and carbon monoxide diffused at the rate of about 1 per cent a day.

